

Dynamical heterogeneity in a model for permanent gels: Different behavior of dynamical susceptibilities

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We present a systematic study of dynamical heterogeneity in a model for permanent gels, upon approaching the gelation threshold. We find that the fluctuations of the self intermediate scattering function are increasing functions of time, reaching a plateau whose value, at large length scales, coincides with the mean cluster size and diverges at the percolation threshold. Another measure of dynamical heterogeneities, i.e. the fluctuations of the self-overlap, displays instead a peak and decays to zero at long times. The peak, however, also scales as the mean cluster size. Arguments are given for this difference in the long time behavior. We also find that non-Gaussian parameter reaches a plateau in the long time limit. The value of the plateau of the non-Gaussian parameter, which is connected to the fluctuations of diffusivity of clusters, increases with the volume fraction and remains finite at percolation threshold.

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I. INTRODUCTION

In the context of the glass transition the concept of dynamical heterogeneities has been very fecund [1–12]. In glassy systems the correlated motion of particles manifest as significant fluctuations around the average dynamics, strongly increasing as the transition is approached. These heterogeneities in the dynamics have been studied quantitatively via the so-called dynamical susceptibility [3], $\chi_4(t) = N(\langle F^2(t) \rangle - \langle F(t) \rangle^2)$, obtained as the fluctuations of a suitable time dependent correlator $F(t)$ (where N is the number of particles and $\langle \dots \rangle$ is the ensemble average). Two quantities are usually considered: The fluctuations of the self intermediate scattering functions (ISF) [6, 13] $\chi_4(k, t) = N[\langle |\Phi_s(k, t)|^2 \rangle - \langle \Phi_s(k, t) \rangle^2]$ usually measured in numerical simulations, and the fluctuations of the time dependent overlap [14–16] $\chi_4^Q(t) = N[\langle q(t)^2 \rangle - \langle q(t) \rangle^2]$, which, first introduced in p -spin glass models [3], has been calculated also within mode coupling theory [3, 13]. For the fluctuations of the overlap, the role of the inverse of the wave vector k is played by the parameter a characterizing the overlap function, which is different from zero only if a particle has moved a distance less than the fixed value a . In usual glassy systems the behavior observed in the dynamical susceptibility is essentially the same despite of different choices of $F(t)$ [4, 6, 13]: $\chi_4(t)$ grows as a function of the time, reaches a maximum and then decreases to a constant, consistently with the transient nature of the dynamical heterogeneities. Some differences in the k dependence of these two quantities were however found in a model for glasses [17].

Recently, dynamical heterogeneities have been studied in other complex systems, such as granular media

[18–21] and attractive colloidal systems [22–26], where behaviors qualitatively similar to that found in glasses are observed. In particular, Ref.[26] reports a systematic study of the dynamic susceptibility in colloidal systems along the attractive glassy line. Typically the dynamical susceptibility, defined as the fluctuations of the self ISF, displays a well pronounced peak. However, in the attraction-dominated limit, the dependence on both time and wave vector markedly differs from that in standard repulsion-dominated systems (hard-sphere limit).

In a recent letter [27] we have studied the behavior of the dynamical susceptibility, χ_4 , defined as the fluctuations of the self ISF, in a model for permanent gel, where bonds are modeled using a finitely extendable non linear elastic (FENE) potential [29, 30] between neighboring particles. It was found that the behaviour of $\chi_4(k, t)$ is drastically different from that found in glasses. In fact it grows in time until it reaches a plateau in the limit of large time t , without decaying to 1. The value of the plateau in the limit of low wave vector, $k \rightarrow 0$, was in fact found to coincide with the mean cluster size. As a consequence, as the system approaches the gel transition (i.e. the percolation threshold), the value of the plateau diverges. For a fixed value of k , the value of the plateau coincides with the mean cluster size up to a linear size of the order of the inverse of k . Therefore, for any $k > 0$ ($k > k_{min}$ in our study), the plateau never diverges: it decreases as k increases and eventually goes to one.

Here we present a systematic study of this FENE model for permanent gels [27]. Moreover, we compare the behavior of the fluctuations of the self ISF and of the self-overlap, and find a marked difference between the two ones. The first one, as mentioned above, is an increasing function of the time and tends to a plateau,

whereas the second one reaches a maximum and then decreases. However, the value of the maximum scales as the value of the plateau of the fluctuations of the self ISF, with the same critical exponent of the mean cluster size.

The reason why these two quantities differ so drastically in the long time limit is the following: the fluctuation of the overlap is related to the correlations between the event that a monomer has moved a distance less than a in a time interval t and the event that another monomer has also moved a distance less than a in the same interval t . In the long time t all particles have moved a distance larger than a therefore such correlations are zero. On the other hand in the long time limit the fluctuation of the self ISF is related to the correlation of the distance separating monomers i and j at time 0 and the distance between the same monomers at time t . This quantity is different from zero if the particles i and j are in the same cluster.

Although the long time limit of the two quantities $\chi_4(k, t)$ and $\chi_4^Q(a, t)$ is different in gels with permanent bonds, they have in common not only the property that plateau and maximum scale in the same way, but also one key feature which is the strong length scale dependence: The peak of the fluctuations of the self part of the overlap and the plateau of the fluctuations of the self ISF decreases strongly as the wave vector k (or $1/a$) increases, which is the sign that clusters of bonded particle dominate the dynamics. The same feature is also valid for strong colloidal gels [31]. This strong length scale dependence of the dynamical susceptibility seems to be the distinctive sign of permanent or strong colloidal gelation, compared with the (attractive or repulsive) glass transition.

Finally, we measure the non-Gaussian parameter α_2 and find that, due to the presence of clusters, it is different from zero also in the long time limit. However, its plateau value, which is connected to diffusivity, remains finite upon approaching the transition.

In Sect.II we introduce the model used and give the details of the numerical simulations. We analyze the self ISF and its fluctuations in Sect.III and the self-overlap and its fluctuations in Sect.IV. The mean squared displacement and the non-Gaussian parameter are discussed in Sect.V, whereas the Sect.VI contains the concluding remarks. Finally, in Appendix A we investigate the static properties of the sol-gel transition, corresponding to the percolation of permanent bonds between particles [32, 33].

II. MODEL AND NUMERICAL SIMULATIONS

We consider a 3d system of N particles interacting with a soft potential given by Weeks-Chandler-Andersen

(WCA) potential [28]:

$$U_{ij}^{WCA} = \begin{cases} 4\epsilon[(\sigma/r_{ij})^{12} - (\sigma/r_{ij})^6 + \frac{1}{4}], & r_{ij} < 2^{1/6}\sigma \\ 0, & r_{ij} \geq 2^{1/6}\sigma \end{cases} \quad (1)$$

where r_{ij} is the distance between the particles i and j .

After the equilibration, particles distant less than R_0 are linked by adding an attractive potential:

$$U_{ij}^{FENE} = \begin{cases} -0.5k_0R_0^2 \ln[1 - (r_{ij}/R_0)^2], & r_{ij} < R_0 \\ \infty, & r_{ij} \geq R_0 \end{cases} \quad (2)$$

representing a finitely extendable nonlinear elastic (FENE). The FENE potential was firstly introduced in Ref.[29] and is widely used to study linear polymers [30]. We choose $k_0 = 30\epsilon/\sigma^2$ and $R_0 = 1.5\sigma$ as in Ref.[30] in order to avoid any bond crossing and to use an integration time step Δt not too small [34]. The introduction of the FENE potential leads to the formation of permanent bonds among all the particles whose distance at that time is smaller than R_0 .

We have performed molecular dynamics simulations of this model: The equations of motion were solved in the canonical ensemble (with a Nosé-Hoover thermostat) using the velocity-Verlet algorithm [35] with a time step $\Delta t = 0.001\delta\tau$, where $\delta\tau = \sigma(m/\epsilon)^{1/2}$ is the standard unit time for a Lennard-Jones fluid and m is the mass of particle. We use reduced units where the unit length is σ , the unit energy is ϵ and the Boltzmann constant k_B is set equal to 1. We use periodic boundary conditions, and average all the investigated quantities over 32 independent configurations of the system.

The temperature is fixed at $T = 2$ and the volume fraction $\phi = \pi\sigma^3 N/6L^3$ (where L is the linear size of the simulation box in units of σ) is varied from $\phi = 0.02$ to $\phi = 0.12$. Using the percolation approach, we identify the gel phase as the state in which there is a percolating cluster [32, 33]. A finite size scaling analysis is presented in the Appendix, showing that this transition is in the universality class of random percolation. We find that the threshold is $\phi_c = 0.09 \pm 0.01$. In particular, we obtain that the cluster size distribution, $n_s \sim s^{-\tau}$ for $\phi = \phi_c$ with $\tau = 2.1 \pm 0.2$, the mean cluster size $S(\phi) = \sum s^2 n_s / \sum s n_s \sim (\phi_c - \phi)^{-\gamma}$ with $\gamma = 1.8 \pm 0.1$, and the connectedness length $\xi \sim (\phi_c - \phi)^{-\nu}$ with $\nu = 0.88 \pm 0.01$. In the following we fix the number of particles, $N = 1000$.

Due to the introduction of bonds, spatial correlations appear at low wave vectors. Although these correlations increase as a function of the volume fraction, the low k limit of the static structure factor $S(k)$ is always small compared to the number of particles, and no phase separation is observed.

III. SELF INTERMEDIATE SCATTERING FUNCTION AND ITS FLUCTUATIONS

Relevant information on the relaxation dynamics over different length scales can be obtained from the self Intermediate Scattering Functions (ISF) $F_s(k, t)$:

$$F_s(k, t) = [\langle \Phi_s(k, t) \rangle] \quad (3)$$

where $\langle \dots \rangle$ is the thermal average over a fixed bond configuration, $[\dots]$ is the average over 32 independent bond configurations of the system, and

$$\Phi_s(k, t) = \frac{1}{N} \sum_{i=1}^N e^{i\vec{k} \cdot (\vec{r}_i(t) - \vec{r}_i(0))} \quad (4)$$

In Fig.1, $F_s(k, t)$ is plotted as a function of t for different ϕ , respectively for $k_{min} = 2\pi/L \sim 0.35$ (main frame) and $k \sim 7$ (inset). At the smallest wave vector, for very low values of the volume fraction, the self ISF decays to zero following an exponential behavior. As the volume fraction is increased towards the percolation threshold, we observe the onset of a stretched exponential decay, $e^{-(t/\tau)^\beta}$, with β decreasing as a function of ϕ (for instance $\beta = 0.75 \pm 0.01$ for $\phi = 0.07$ and $\beta = 0.58 \pm 0.02$ for $\phi = 0.085$). The cluster size distribution has started to widen towards the percolation regime (see Appendix), and therefore, over sufficiently large length scales, the behavior of $F_s(k, t)$ is due to the contribution of different relaxation processes, characterized by different relaxation times, whose superposition produces a detectable deviation from an exponential law. Near the transition threshold the long time decay is characterized by a power law behavior, indicating that the relaxation over this length scale is controlled by the formation of the percolating cluster, with a critically growing relaxation time. If the volume fraction increases further, the decay becomes slower and slower, showing a logarithmic behavior. These features of the dynamics well reproduce the experimental findings [36]. Moreover they agree with results obtained via numerical simulations of different gelation models [37–39]. At large wave vectors (see Inset of Fig.1) and low volume fractions, $F_s(k, t)$ decays to zero as $e^{-(t/\tau)^2}$ (continuous curves in figure), corresponding to the ballistic regime of particle motion.

From the self ISF we calculate the structural relaxation time, $\tau(k, \phi)$, defined as the time for which $F_s(k, \tau(k)) \simeq 0.1$. In Fig.2, $\tau(k, \phi)$ is plotted for different values of k as a function of the volume fraction ϕ . For $k = k_{min}$, we find that $\tau(k_{min}, \phi)$ is well fitted by a power law diverging at the gelation threshold with an exponent $f \sim 1.22$. Increasing k , no divergence is observed at the threshold, signalling that no structural arrest occurs over length scales less than the box size, L .

In Fig.3 and in its inset we plot respectively $k^2\tau(k, \phi)$ and $k\tau(k, \phi)$ as a function of the wave vector for different volume fractions. The inset of Fig.3 shows that $\tau \sim 1/k$ for large wave vectors, reflecting the ballistic diffusion

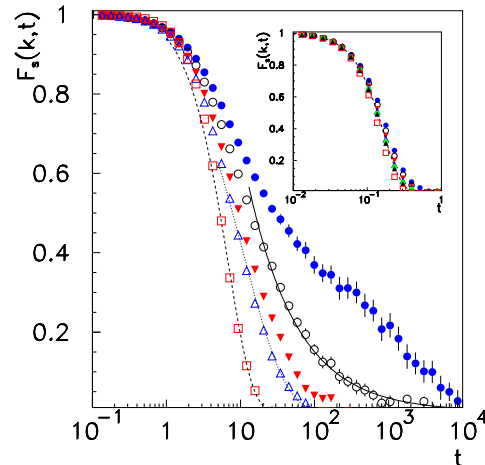


FIG. 1: (Color online) **Main frame:** Self ISF for $\phi = 0.02, 0.07, 0.08, 0.09, 0.1$ (from bottom to top) and $k \sim 0.35$ as a function of time t . The lines are fitting curves: For $\phi \ll \phi_c$ the decay is well fitted by an exponential behavior (dashed line); if ϕ approaches to ϕ_c a stretched exponential decay appears, with $\beta = 0.75 \pm 0.01$ for $\phi = 0.07$ (dotted line). For $\phi = 0.09$ the decay is well fitted by a power law $\sim t^{-c}$ with $c = 0.65 \pm 0.03$ (full line). **Inset:** Self ISF for $k \sim 7$ and the same volume fractions of main frame.

for short times (see Sect.V). Interestingly in the limit of small wave vectors $k^2\tau$ does not tend to a constant. This unusual result is essentially due to the fact that the non-Gaussian parameter [40], $\alpha_2(t) = \frac{3\Delta r^4(t)}{5(\Delta r^2(t))^2} - 1$, is non zero in the long time limit, as discussed in details in Sect.V. In this case the Gaussian approximation of the probability distribution of particle displacements is not valid, and the self ISF $F_s(k, t)$ cannot be written as a Gaussian even in the limit of small wave vector.

We now analyze and discuss the behaviour of the fluctuations of the self ISF, i.e. the dynamical susceptibility:

$$\chi_4(k, t) = N \left[\langle |\Phi_s(k, t)|^2 \rangle - \langle \Phi_s(k, t) \rangle^2 \right]. \quad (5)$$

In Fig.4 $\chi_4(k, t)$ is plotted for $k = k_{min}$ and different volume fractions. Differently from the behavior typically observed in glassy systems, we find that, for $\phi < \phi_c$, $\chi_4(k, t)$ is a monotonically increasing function of the time tending to a plateau in a time of the order of the relaxation time $\tau(k_{min})$. The value of the plateau diverges as the mean cluster size as the percolation threshold is approached [27]. For $\phi \geq \phi_c$ the system is out of equilibrium, $\chi_4(k, t)$ continues increasing as a function of time, without reaching any asymptotic value within the simulation time. We briefly discuss the main arguments explaining the above result, presented in Ref [27], where it was in fact shown that, for $k \rightarrow 0$ and $t \rightarrow \infty$, the dynamical susceptibility $\chi_4(k, t)$ tends to the mean cluster size. We define $\chi_{as}(k, \phi) \equiv \lim_{N \rightarrow \infty} \lim_{t \rightarrow \infty} \chi_4(k, t)$.

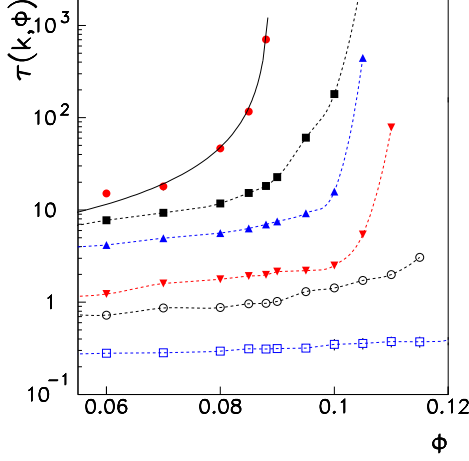


FIG. 2: (Color online) Structural relaxation time $\tau(k, \phi)$ as a function of the volume fraction, for wave vector $k \sim 0.35, 0.6, 1.0, 2.0, 3.0, 7.0$ (from top to bottom). The full line is the fitting curve: $\tau(k_{min}, \phi) \sim (\phi_c - \phi)^{-f}$, with $f \sim 1.22$. Dashed lines are eye guides.

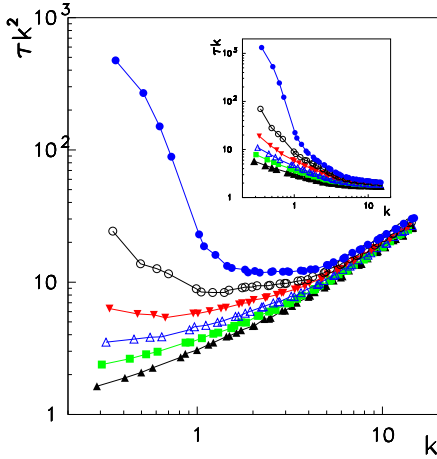


FIG. 3: (Color online) **Main frame:** $k^2 \tau(k, \phi)$ as a function of k , for $\phi = 0.05, 0.06, 0.07, 0.08, 0.09, 0.1$ (from bottom to top). **Inset:** $k \tau(k, \phi)$ as a function of k for the same volume fractions of main frame.

Being $\lim_{t \rightarrow \infty} \langle \Phi_s(k, t) \rangle = 0$, we have

$$\chi_{as}(k, \phi) = \lim_{N \rightarrow \infty} \frac{1}{N} \left[\sum_{i,j=1}^N C_{ij}(k) \right] \quad (6)$$

where $C_{ij}(k) = \lim_{t \rightarrow \infty} \langle e^{i\vec{k} \cdot (\vec{r}_i(t) - \vec{r}_j(t))} e^{-i\vec{k} \cdot (\vec{r}_i(0) - \vec{r}_j(0))} \rangle = |\langle e^{i\vec{k} \cdot (\vec{r}_i - \vec{r}_j)} \rangle|^2$. Here we have used the fact that, for large enough time t , the term $e^{-i\vec{k} \cdot (\vec{r}_i(t) - \vec{r}_j(t))}$ is statistically

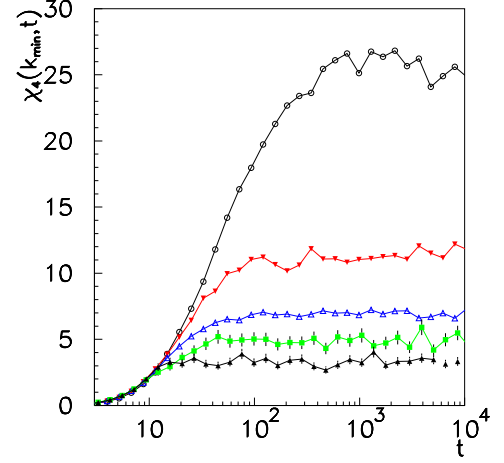


FIG. 4: (Color online) Dynamical susceptibility, $\chi_4(k, t)$, as a function of time for $k = k_{min}$ and different volume fractions $\phi = 0.05, 0.06, 0.07, 0.08, 0.09$ (from bottom to top).

independent from $e^{-i\vec{k} \cdot (\vec{r}_i(0) - \vec{r}_j(0))}$, so that we can factorize the thermal average. We separate the sum over connected pairs ($\gamma_{ij} = 1$, i.e. pairs belonging to the same cluster) and disconnected pairs ($\gamma_{ij} = 0$, i.e. pairs belonging to different clusters), so that:

$$\chi_{as}(k, \phi) = \lim_{N \rightarrow \infty} \frac{1}{N} \left[\sum_{i,j=1}^N \gamma_{ij} C_{ij}(k) \right] + \frac{1}{N} \left[\sum_{i,j=1}^N (1 - \gamma_{ij}) C_{ij}(k) \right] \quad (7)$$

If particles i and j are not connected, for any fixed value of $k > 0$, the quantity $C_{ij}(k)$ is $O(1/N^2)$ [41]. As there are at most N^2 disconnected pairs, the second term of the r.h.s. of Eq.(7) is $O(1/N)$, and can be neglected in the thermodynamical limit.

For $\phi < \phi_c$, clusters will have at most a linear size of order ξ , so that the relative distance $|\vec{r}_i - \vec{r}_j|$ of connected particles will be smaller than ξ . Therefore we have $\lim_{k \rightarrow 0} \gamma_{ij} C_{ij}(k) = \gamma_{ij}$ and

$$\lim_{k \rightarrow 0} \chi_{as}(k, \phi) = \lim_{N \rightarrow \infty} \frac{1}{N} \left[\sum_{i,j=1}^N \gamma_{ij} \right] = S, \quad (8)$$

where S is the mean cluster size. As shown in Ref.[27], numerical data confirm this result.

In Fig.5 $\chi_4(k, \phi)$ is plotted for $\phi = 0.09$ and different wave vectors. For each value of the wave vector, $\chi_4(k, \phi)$ reaches a plateau after a characteristic time of the order of the relaxation time $\tau(k)$. The asymptotic value $\chi_{as}(k, \phi_c)$ at low wave vectors follows a scaling behavior as a function of k (Inset of Fig.5): at the transition threshold the exponent is 2.03 ± 0.02 , consistent, within the numerical accuracy, with the prediction $2 - \eta$

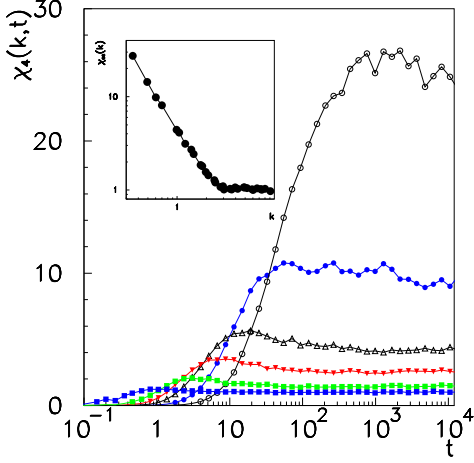


FIG. 5: (Color online) **Main Frame:** Dynamical susceptibility, $\chi_4(k, t)$, as a function of time for $\phi = 0.09$ and $k = 0.35, 0.61, 0.99, 1.40, 2.10, 3.96$ (from top to bottom). **Inset:** Asymptotic values of the susceptibility, $\chi_{as}(k, \phi_c)$ as a function of the wave vector k . Data are fitted with a power law $\sim k^{-2.03 \pm 0.02}$, in agreement with the exponent $2 - \eta$ of random percolation.

of random percolation [42]. This result shows that if one varies the wave vector k (and $2\pi/k > \sigma$) the dynamical susceptibility is able to detect the self-similarity of the structure of the system due to the percolation transition. Using scaling arguments [27], we can write $\chi_{as}(k, \phi) = k^{\eta-2} f(k\xi)$ where $f(z)$ is a function, which tends to a constant for small z , whereas it behaves as $z^{\gamma/\nu}$ for large values of z . As shown in Ref.[27], data support this scenario. All these results coherently show how in the present system the asymptotic value of the dynamical susceptibility can be related to the cluster size. Not only our results indicate that the percolation exponents can be measured in a direct way, by developing techniques to measure the dynamical susceptibility, but they also state that the asymptotic value of the dynamical susceptibility plays the same role as the static scattering function near the liquid gas critical point.

IV. SELF OVERLAP AND ITS FLUCTUATIONS

In the context of glassy systems, a time-dependent order parameter was introduced [14–16], which measures the number of “overlapping” particles in two configurations separated by a time interval t ,

$$\begin{aligned} q(t) &= \frac{1}{N} \int d\vec{r}_1 d\vec{r}_2 \rho(\vec{r}_1, 0) \rho(\vec{r}_2, t) w(|\vec{r}_1 - \vec{r}_2|) \\ &= \frac{1}{N} \sum_i \sum_j w(|\vec{r}_i(0) - \vec{r}_j(t)|), \end{aligned} \quad (9)$$

where $\rho(\vec{r}, t) = \sum_i \delta(\vec{r} - \vec{r}_i(t))$ is the density in \vec{r} at time t , and $w(|\vec{r}_1 - \vec{r}_2|)$ is an “overlap” function that is 1 for $|\vec{r}_1 - \vec{r}_2| \leq a$ and zero otherwise [43].

In Ref.[4] the authors separate q into self and distinct components, $q(t) = q_S(t) + q_D(t)$. The self part is given by:

$$q_S(t) = \frac{1}{N} \sum_i w(|\vec{r}_i(0) - \vec{r}_i(t)|) \quad (10)$$

which corresponds to terms of Eq.(9) with $i = j$, and measures the number of particles that move less than a distance a in a time interval t . In Ref.[4] it was shown that on average the dominant term is given by the self part.

Here we measure $Q_S(t) = [\langle q_S(t) \rangle]$ for two choices of a , 0.15 and 3, respectively corresponding to $1/a \gg k_{min}$ and $1/a \simeq k_{min}$. $Q_S(t)$ is plotted in Fig.6 for different values of the volume fraction. We have verified by numerical calculations that for small enough a , the relevant contribution to $Q(t) = [\langle q(t) \rangle]$ is given by $Q_S(t)$, since the probability that a particle replaces within a radius a another particle is small. For all the values of a and of ϕ considered, $Q_S(t)$ at long times is well fitted by a power law.

Another interesting method to investigate the spatially heterogeneous dynamics, generally used in glassy systems, is the measure of the dynamical susceptibility obtained by the fluctuations of the time dependent overlap [14–16] $\bar{\chi}_4^Q(a, t) = N[\langle q(t)^2 \rangle - \langle q(t) \rangle^2]$, where $q(t)$ is given by Eq.(9). In glassy systems this quantity essentially presents the same features as the fluctuations of the self ISF.

Here we measure the fluctuations of the self part of the overlap:

$$\chi_4^Q(a, t) = N[\langle q_S(t)^2 \rangle - \langle q_S(t) \rangle^2], \quad (11)$$

for different choices of a , ranging from 0.15 to 3. In Fig.7 we plot $\chi_4^Q(a, t)$ for $a = 3$ and different values of ϕ .

We see that differently from the fluctuations of the self ISF, here $\chi_4^Q(a, t)$ displays a peak, whose value increases and diverges as the the gel transition is approached. Indeed, the value of the peak differ from the value of the plateau $\chi_{as}(k_{min})$ only for a constant factor (see inset of Fig.7) and therefore scales with the same exponent of the mean cluster size γ [44]. Even if the long time limit of $\chi_4^Q(a, t)$ is strongly different from the one observed in $\chi_4(k, t)$, both fluctuations manifest a strong dependence on length scale. In fact, the peak of $\chi_4^Q(a, t)$ strongly decreases as a decreases (see Fig.8). This may be interpreted as a sign that clusters of bonded particle dominate the dynamics.

Our data and these considerations suggest that heterogeneities detected by $\chi_4^Q(a, t)$ are due to the presence of clusters. However, despite the permanent nature of clusters, fluctuations of the self overlap $\chi_4^Q(a, t)$ decay to zero in the long time limit. This is due to the form of

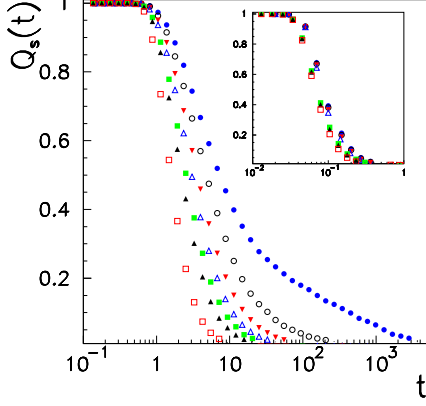


FIG. 6: (Color online) **Main frame:** Self overlap, $Q_s(t)$, for $a = 3$ and different volume fractions from $\phi = 0.02, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1$ (from bottom to top). **Inset:** Self overlap for the same values of ϕ of main frame and $a = 0.15$.

the overlap function $w(|\vec{r}_i(0) - \vec{r}_i(t)|)$, which is zero when a particle has moved a distance greater than a . Therefore two particles in the same cluster will contribute to $\chi_4^Q(a, t)$, if the center of mass of the cluster has moved a distance less than a . In fact, when the cluster moves a distance larger than a , due to the form of the overlap function, the contribution to $\chi_4^Q(a, t)$ vanishes. Therefore we expect that for $1/a \simeq k_{min}$ the peak is proportional to the mean cluster size, and occur at a time t^* of the order of the time in which the center of the typical cluster of dimension ξ has moved a distance of the order of a .

V. MEAN SQUARE DISPLACEMENT AND THE NON-GAUSSIAN PARAMETER

Finally we have measured the mean square displacement (MSD)

$$\Delta r^2(t) = \frac{1}{N} \sum_{i=1}^N [\langle |\vec{r}_i(t) - \vec{r}_i(0)|^2 \rangle], \quad (12)$$

where $\vec{r}_i(t)$ is the position of the i -th particle at the time t . In the main frame of Fig.9 the MSD is shown for different volume fractions. Due to the Newtonian dynamics, we find at very short time a ballistic behaviour, $\Delta r^2(t) \propto t^2$, followed by a crossover to a diffusive regime $\Delta r^2(t) \propto t$. The long time diffusive regime is always recovered for all the volume fractions considered, indicating that even at the percolation threshold this quantity is dominated by free motion of particles or clusters. Accordingly, no divergence of the inverse diffusion coefficient is found at the percolation threshold, where the

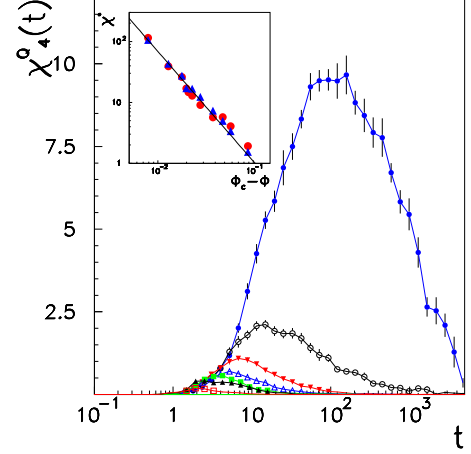


FIG. 7: (Color online) **Main frame:** Fluctuations of the self-overlap, $\chi_4^Q(a, t)$, for $a = 3$ and $\phi = 0.02, 0.05, 0.06, 0.07, 0.08, 0.09, 0.1$ (from bottom to top). **Inset:** $10 \cdot \chi_4^Q(t^*)$ (circles) for $a = 3$ and $\chi_{as}(k_{min}, \phi)$ (triangles) as a function of $(\phi_c - \phi)$.

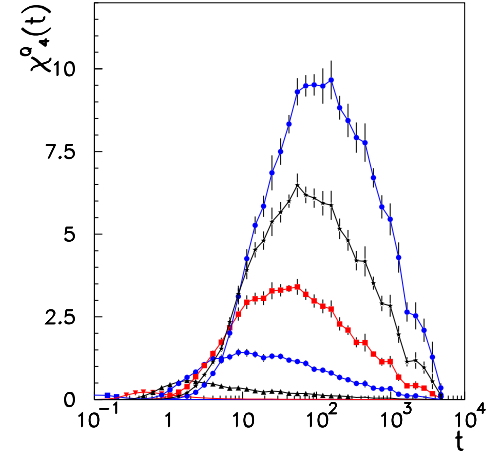


FIG. 8: (Color online) **Main frame:** Fluctuations of the self-overlap, $\chi_4^Q(a, t)$, for $\phi = 0.1$ and $a = 0.15, 0.5, 1, 1.5, 2, 2.5, 3$ (from bottom to top).

numerous small size clusters continue to diffuse into the large mesh of the spanning cluster.

We have also evaluated the MSD of the clusters and extracted their diffusion coefficient as a function of the cluster size s . In particular we obtained that for $\phi = \phi_c$, $D(s)$ for large s is fitted by a power law s^{-h} with $h = 1.0 \pm 0.1$ (see inset of Fig.9). Following [38] we expect $D(s) \sim 1/s^{(d-2+f/\nu)/d_f}$, where $d = 3$ is the Euclidean dimension, f is the exponent which gives the di-

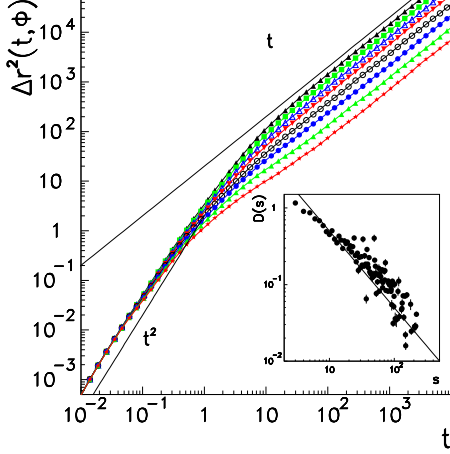


FIG. 9: (Color online) **Main frame:** Mean square displacement for $\phi = 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.11, 0.12$. **Inset:** Diffusion coefficient, $D(s)$, as a function of the cluster size s for $\phi = \phi_c$.

vergence of the viscosity, $\nu \sim 0.88$ is the critical exponent which gives the divergence of the connectedness length (see Appendix), and $d_f \sim 2.4$ is the fractal dimension of the spanning cluster at the threshold (see Appendix). Using these values we obtain a prediction for the exponent, which gives the divergence of the viscosity at the threshold $f = \nu(hd_f - d + 2) \sim 1.23$ in agreement within the errors with our data for the structural relaxation time (see Sect.III and Fig.2).

In order to characterize the displacement of particles we have calculated the self part of the Van-Hove function [45]:

$$G_s(r, t) = \frac{1}{N} \left[\left\langle \sum_{i=1}^N \delta(r - |\vec{r}_i(t) - \vec{r}_i(0)|) \right\rangle \right]. \quad (13)$$

If the motion of particles is diffusive with a diffusion coefficient D , $G_s(r, t) = (1/4\pi Dt)^{3/2} e^{-(r^2/4Dt)}$, where r is the distance traveled by a particle in a time t . In the inset of Fig.10 we plot the self van Hove function for a fixed volume fraction at different times. Our results indicate that for short times and short distances the function is well fitted by a Gaussian. For long distances and long times, the van Hove function is well fitted by an exponential decay. An exponential decay has been observed in different glassy systems for intermediate times [46].

The deviation from the Gaussian distribution at long times, observed in our system, indicates that some particles move faster than others, due to the presence of clusters. Particles belonging to different clusters have a different diffusion coefficient depending on the cluster size. As a consequence we suggest that, in the diffusive regime, $G_s(r, t)$ does not have a Gaussian form, but it is

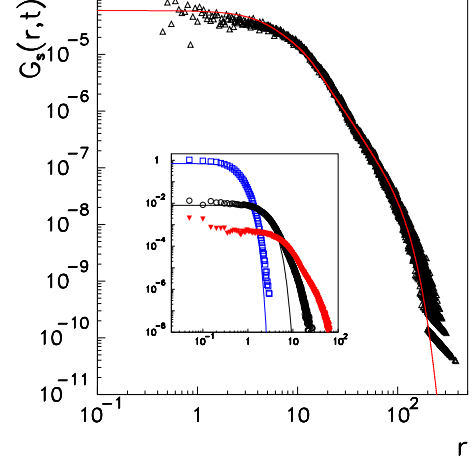


FIG. 10: (Color online) **Main frame:** The self part of the Van-Hove distribution for $\phi = 0.09$ and time $t = 1285.02$. The continuous line is obtained from the diffusion coefficient of clusters using Eq.(14). **Inset:** The self part of the Van-Hove distribution for $\phi = 0.09$ and different times $t = 0.469, 6.739, 93.199$ (from left to right). The lines are Gaussian fitting functions.

instead given by a superposition of Gaussians

$$G_s(r, t) = \sum_s s n_s \left(\frac{1}{4\pi D(s)t} \right)^{3/2} e^{-r^2/4D(s)t}, \quad (14)$$

where $D(s)$ is the diffusion coefficient of cluster of size s and n_s is the cluster size distribution.

In Fig.10 we compare our data with $G_s(r, t)$ calculated using Eq.(14) and $D(s)$ obtained from the simulations. As we can see in figure, data are in good agreement with our predictions, provided that time is sufficiently long for clusters diffusing with diffusion coefficient $D(s)$.

In agreement with this finding, the non-Gaussian parameter, which is a measure of the departure from the Gaussian behaviour of the probability distribution of the particle displacements, does not go to zero at long times. The non-Gaussian parameter is defined as [40]:

$$\alpha_2(t) = \frac{3\Delta r^4(t)}{5(\Delta r^2(t))^2} - 1, \quad (15)$$

where $\Delta r^4(t) = \frac{1}{N} \sum_{i=1}^N [|\vec{r}_i(t) - \vec{r}_i(0)|^4]$ and it is zero if the probability distribution of the particle displacements is Gaussian.

In glassy systems [2], (i) on the time scale at which the motion of the particles is ballistic, α_2 is zero; ii) upon entering the time scale of the β relaxation, α_2 starts to increase; iii) on the time scale of the α relaxation, α_2 decreases to its long time limit, zero. The maximum value of α_2 increases with decreasing temperature, signalling that the dynamics becomes more heterogeneous.

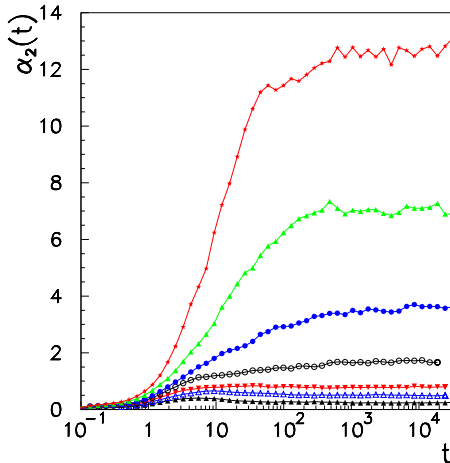


FIG. 11: (Color online) Non-Gaussian parameter, $\alpha_2(t)$ as a function of time t for $\phi = 0.05, 0.06, 0.07, 0.08, 0.09, 0.1, 0.12$.

In the present model for permanent gels, we find that i) as in glasses, α_2 is always zero on the time scale at which the motion of the particles is ballistic; ii) it tends in the long time limit to a plateau value, which increases with increasing volume fraction; iii) at low volume fraction, α_2 has a maximum at intermediate times, which disappears upon approaching the gelation threshold; iv) no critical behaviour is observed at the gelation threshold.

Within our interpretation the asymptotic value of the non-Gaussian parameter, using Eq.(14) may be written in the following form:

$$\alpha_2^{as} = \frac{\sum_s s n_s D^2(s)}{(\sum_s s n_s D(s))^2} - 1 = \frac{\overline{D^2} - \overline{D}^2}{\overline{D}^2}, \quad (16)$$

where, for each bond configuration, $\overline{(\dots)}$ is the average over the cluster distribution. We have verified that α_2^{as} coincides with $\frac{\overline{D^2} - \overline{D}^2}{\overline{D}^2}$ within the errors. Hence our results indicate that the non-Gaussian parameter tends to a plateau given by the ratio of two quantities, which both have no critical behaviour at the percolation threshold. In summary, as the fluctuations of the self ISF, the non-Gaussian parameter does not decay to zero in the long time limit, due to the presence of permanent clusters. However, the main contribution to α_2 comes from the numerous finite clusters (the bigger the cluster, the lower its diffusion coefficient $D(s)$, and consequentially its contribution to α_2), so that no criticality approaching the percolation threshold is observed in the non Gaussian parameter.

VI. CONCLUSION

We have presented a molecular dynamics study of a model for permanent gels and investigated its static and dynamical properties. Usually the sol-gel transition, marked by the divergence of viscosity and the onset of an elastic modulus, is interpreted in terms of the appearance of a percolating cluster of monomers linked by bonds [32, 33, 42]. While the viscosity and the elastic modulus can be measured directly, usually the experimental determination of percolative properties needs the manipulation of the sample (for a review see [47] and references therein), i.e. the sample is dissolved in a known quantity of solvent in such a way that each cluster is separated from the others. For the first time our results identify the thermodynamical observable associated with the cluster properties in a gelling system, and, via the measure of the fluctuations of the self ISF, allow to obtain the critical exponents without such a manipulation of the sample.

In our model the formation of permanent bonds between the particles leads to a percolation transition in the universality class of random percolation. The percolation threshold coincides with the gelation threshold, marked by the slowing down of dynamics on length scale of the whole system. We have found that the behavior of the self ISF in the sol phase and near the threshold is in agreement with typical experiments on gelling systems. In chemical gels the onset of a stretched exponential decay is typically associated to the wide cluster size distribution close to the gelation threshold, producing a wide distribution of relaxation times. At the percolation threshold, the longest relaxation time diverges due to the critical growing of the percolation correlation length, producing a long time power law decay. Our results confirm this picture but new insights are obtained with a study of the dynamical heterogeneities, in terms of fluctuations of different correlation functions. In the present model for permanent gels, the fluctuations of the self-overlap present always a peak, whereas the fluctuations of the self ISF are monotonically increasing with time. Differently from glassy systems, the fluctuations of the self ISF tend in the long time limit to a plateau, whose value, for the lowest wave vector, coincides with the mean cluster size. The behavior of the non-Gaussian parameter as a function of time is qualitatively similar: in the long time limit it reaches a plateau, due to the contribution of particles belonging to different clusters with a size dependent diffusion coefficient. Nevertheless, the value of the plateau does not diverge at the gelation transition, being dominated by the presence of small clusters with finite diffusivity.

This study has shed some light on the differences between the dynamics and the dynamical heterogeneities in glasses and chemical gels. We have been able to clarify that, when clusters of bonded particles are present, different time correlators can deliver very different information whereas in the studies on glasses they are often used interchangeably. On this basis, these findings have

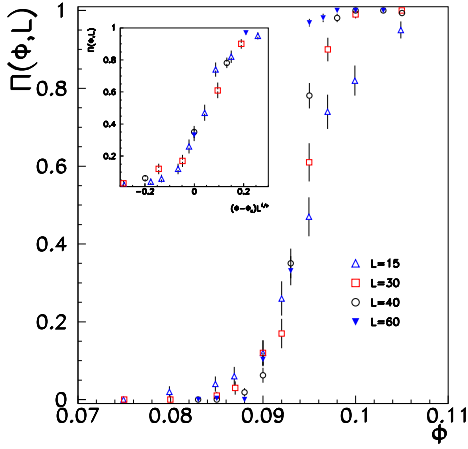


FIG. 12: (Color online) **Main frame:** Percolation probability $\Pi(\phi, L)$ as a function of the volume fraction ϕ for boxes of size $L = 15, 30, 40, 60$. **Inset:** Data collapse obtained plotting $\Pi(\phi, L)$ versus $(\phi - \phi_c)L^{1/\nu}$ with $\nu = 0.88$ and $\phi_c = 0.09$.

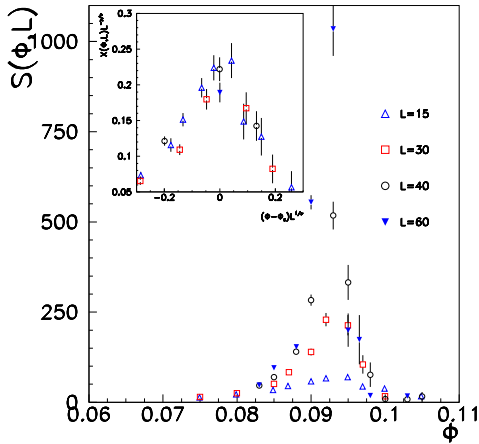


FIG. 13: (Color online) **Main frame:** Mean cluster size $S(\phi, L)$ as a function of the volume fraction ϕ for boxes of the same sizes of Fig. 12. **Inset:** Data collapse obtained plotting $S(\phi, L)L^{-\gamma/\nu}$ versus $(\phi - \phi_c)L^{1/\nu}$ with $\nu = 0.88$, $\phi_c = 0.09$ and $\gamma = 1.85$.

interesting implications for the study of gels due to non-permanent bonds, as in the case of colloidal gels. In fact, our study also indicate a possible way to discriminate between a gel-like behaviour and a glass-like behaviour in these systems. Our results strongly suggest that, if heterogeneities are due to clusters of particles connected by permanent (or persistent) bonds, as in permanent (or colloidal) gels, the behavior of the “time-dependent or-

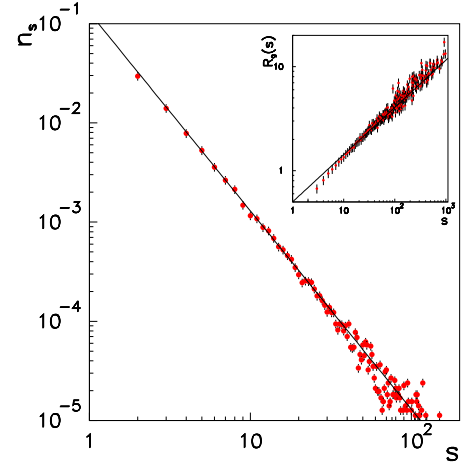


FIG. 14: (Color online) **Main frame:** Average number of clusters (per particle) with mass s versus s at ϕ_c for $L = 40$. The full line is a power law, $s^{-\tau}$, with fitting parameter $\tau = 2.1$. **Inset:** Radius of gyration, R_g , as a function of the mass s of clusters at ϕ_c for $L = 40$. The full line is a power law, s^{1/d_f} , with fitting parameter $d_f = 2.4$.

der parameter”, whose fluctuations reveal the presence of heterogeneities in the dynamics, may be quite different. However both quantities show a strong length scale dependence (both strongly decrease as k or $1/a$ increase), which seems to be the distinct sign of (permanent or colloidal) gelation compared with the (attractive or repulsive) glass transition [31]. This result is confirmed by a recent work [48], where it has been found that, in a model for colloidal gels, at low volume fraction, the fluctuations of the self ISF for small wave vector display a dependence on time, which is dramatically different from the one found at higher volume fraction [23, 26] in the glassy regime. As a final remark, it is interesting to note that in the model here discussed the dynamical susceptibility is similar to that observed in a spin glass model with quenched interactions [49], suggesting a possible common description of the phase transition involved, as also proposed elsewhere [50].

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APPENDIX A: PERCOLATION TRANSITION

In this Appendix, with a finite size scaling analysis, the percolation threshold and the critical exponents are obtained. We find that the percolation of permanent bonds, corresponding to the sol-gel transition [32, 33], is in the universality class of random percolation.

Varying the volume fraction ϕ , we have measured the

percolation probability, $\Pi(\phi)$ (defined as the average number of configurations where a percolating cluster is found), the cluster size distribution, n_s , and the mean cluster size $S(\phi) = \sum s^2 n_s / \sum s n_s$. For each volume fraction we have used simulation boxes of different size L and, from a standard finite size scaling analysis [42], we have obtained the percolation threshold ϕ_c , and the critical exponents ν (which governs the power law divergence of the connectedness length $\xi \sim |\phi - \phi_c|^{-\nu}$ as the transition threshold is approached from below) and γ (which governs the power law divergence of the mean cluster size $S \sim |\phi - \phi_c|^{-\gamma}$). The percolation threshold and the critical exponents obtained from the data showed in Figs 12 and 13, are respectively $\phi_c = 0.09 \pm 0.01$, $\nu = 0.88 \pm 0.05$ and $\gamma = 1.85 \pm 0.05$. The cluster size distribution n_s

for $\phi = \phi_c$, shown in main frame of Fig. 14, follows a power law behavior $n_s \sim s^{-\tau}$ with a Fisher exponent $\tau = 2.1 \pm 0.2$.

Finally in the inset of Fig.14 the radius of gyration R_g as a function of the mass s of clusters is plotted. The data are well fitted by a power law with exponent $1/d_f = 0.42 \pm 0.03$ (full line in figure) which gives $d_f = 2.4 \pm 0.1$ in agreement with the fractal dimension of the random percolation clusters in $3d$, $d_f \simeq 2.5$. The measured values of the critical exponents satisfy the hyper-scaling relations ($2\beta + \gamma = \nu d$, $d_f = d - \beta/\nu$, and $\tau = 2 + (d - d_f)/d_f$ [42]), and are in good agreement with those of the $3d$ random percolation ($\nu = 0.88$, $\gamma = 1.80$ and $\tau = 2.18$ [42]).

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$$\langle e^{-i\vec{k}\cdot(\vec{r}_i-\vec{r}_j)} \rangle = \frac{1}{N} \int d^3\vec{r} e^{-i\vec{k}\cdot\vec{r}} \rho[h_{ij}(\vec{r}) + 1], \quad (\text{A1})$$

where $\rho = N/V$, $h_{ij}(\vec{r}) + 1 = g_{ij}(\vec{r})$ and $(1/V)g_{ij}(\vec{r})$ gives the probability density of finding the particle i in \vec{r} , given the particle j in the origin. For disconnected pairs, in the thermodynamic limit ($N \rightarrow \infty$ and $L \rightarrow \infty$ leaving the density ρ constant) the integral in Eq.(A1) remains finite for any finite fixed k , so that the l.h.s. of Eq. (A1) is $O(1/N)$. In fact the first term, the Fourier transform of the correlation function $h_{ij}(\vec{r})$, is finite when $L \rightarrow \infty$ since $h_{ij}(\vec{r})$ decays to zero at a finite distance. The second term, the modulus of the Fourier transform of 1, is not larger than $8/|k_x k_y k_z|$, and consequently remains finite when $L \rightarrow \infty$. The quantity $C_{ij}(k)$, being the square modulus of the l.h.s. of Eq. (A1), is therefore $O(1/N^2)$.

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ter a is usually chosen ~ 0.3 . The reasons of this choice are discussed in Ref.[4].

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$$\chi_4^Q(a, t) \sim \sum_s n_s s^2 (\langle w^2(r_{CM}(s, t)) \rangle - \langle w(r_{CM}(s, t)) \rangle^2),$$

where $r_{CM}(s, t)$ is the displacement of any cluster of size s at the time t . In principle $f(s, t) = \langle w^2(r_{CM}(s, t)) \rangle - \langle w(r_{CM}(s, t)) \rangle^2$ depends on the cluster size s . If $f(t, s)$, for a given a , displays, at a time t^* , a peak whose value does not depend on the cluster size s , we obtain that $\chi_4^Q(t^*)$ is proportional to the mean cluster size.

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